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(54) **A steel composition for the production of cold rolled multiphase steel products**

(57) The present invention is related to a steel composition intended to be used in a process comprising a cold rolling step, for the production of uncoated, electro-galvanised or hot dip galvanised TRIP steel products, said composition being characterised by a specific addition of phosphorus. The latter is added in order to reach the desired mechanical properties (high tensile

strength in combination with high elongation) while keeping a good weldability by sufficiently reducing the carbon content. The invention is further related to a process for producing a steel product, and to said steel product obtained, said product having the composition of the invention.

**EP 1 431 406 A1**

## Description

Field of the invention

5 [0001] The present invention is related to a steel composition comprising phosphor, to be used for the production of TRIP steel products. The invention is equally related to the process of production of said products, and to the end products themselves.

State of the art

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[0002] In the automotive industry there is a need for weight reduction, which implies the use of higher strength materials in order to be able to decrease the thickness of the parts without giving up safety and functional requirements. Ultra high strength steel (UHSS) sheet products and in particular TRIP steel products, showing a remarkable combination of high strength and good formability, can provide the solution for this problem. Additionally, an increased corrosion resistance of these steel sheet products by means of electro or hot dip galvanising, is frequently asked for.

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[0003] Several documents are describing such UHSS products. EP-A-1096029 is related to the production of a tempered martensite TRIP steel, whose chemical composition is silicon-manganese based and contains (in wt%) 0.05-0.20% C, 0.3-1.8% Si and 1.0-3.0% Mn as well as one or more of the following additions (in wt%): 0.05-1% Cr+Mo, ≤0.003% B, 0.01-0.1% Ti+Nb+V and ≤0.01% Ca+REM. The cold rolling production process consists of three consecutive annealing steps. In the first step, the sheet is completely austenised during at least 5 seconds and subsequently rapidly cooled (>10°C/s) below the Ms (Martensite start) temperature in order to produce lath martensite. The second and third step are combined in a continuous annealing or galvanising line and consist of reheating the sheet in the intercritical region ( $Ac_1 < T < Ac_3$ ) during 5 to 120 seconds, cooling (>5°C/s) to 500°C or lower and then subjecting the sheet to a galvanising or galvannealing treatment. There are two main drawbacks associated with this invention. The first one being the additional annealing step that is required to produce the lath martensite starting micro-structure. This extra process step will not only increase the total processing cost, but it will also complicate logistics as well as weldability at the entrance of the continuous annealing or hot dip galvanising line. Cracks that are initiated in the weld or heat affected zone, will easily propagate into the hard and brittle martensitic structure, leading to a high risk on complete rupture of the weld between two coils. The second major drawback is related to the rather high Si content in these steels. From about 0.5% Si on, these high Si contents are well known to provoke problems as to surface quality because of the presence of Si-oxides which after pickling create a surface with irregular and very high roughness. Moreover, in view of corrosion protection, hot dip galvanising of such a high Si-containing substrate in general leads to insufficient surface appearance for automotive applications, with moreover a very high risk on the presence of bare spots on the surface.

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[0004] EP-A-0922782 also describes the production of a cold rolled Si-Mn based TRIP steel which contains (in wt%) 0.05-0.40% C, 1.0-3.0% Si, 0.6-3.0% Mn, 0.02-1.5% Cr, 0.01-0.20% P and 0.01-0.3% Al. As opposed to the previous invention, this product does not require the use of an additional annealing step. Cr is added to the analysis in order to retard the bainite formation and promote acicular ferrite and martensite formation as it is thought by the inventors that bainite is detrimental to the crushing behaviour in Si-Mn based TRIP steels. P is added to avoid pearlite formation and to increase the strength of the ferritic phase. The maximal P content is limited to 0.2% because of weldability. The high Si content in this invention will however again impair hot dip galvanisability resulting in an insufficient surface appearance and a very high risk on bare spots. The occurrence of red scale which is difficult to remove, on the hot strip, due to the higher Si content, is also expected to cause processing difficulties.

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[0005] EP-A-0796928 describes the production of an Al-based Dual Phase steel which contains (in wt%) 0.05-0.3% C, 0.8-3.0% Mn, 0.4-2.5% Al and 0.01-0.2% Si. Additionally the steel can contain one of the following elements (in wt%) <0.05% Ti, <0.8% Cr, <0.5% Mo, <0.5% Ni, <0.05% Nb and <0.08% P. After cold rolling with a reduction rate higher than 40%, the material is intercritically annealed at temperatures between 740 and 850°C and subsequently cooled at a cooling rate of 10 to 50 K/s to the Zn-bath temperature. As compared to both previous analyses, the latter, nearly Si-free analysis, readily allows the steel to be hot dip galvanised and avoids the formation of the detrimental red scale. However, Al, as opposed to Si, does not produce a strong solid solution strengthening effect. This implies the use of rather high Al-contents in order to reach medium high strength levels (e.g.  $R_m = 700\text{MPa}$ ). These high Al levels are however known to cause stickers during continuous casting and impair weldability due to the presence of Al-oxides in the welded area. This is especially detrimental for the crash behaviour of welded structures. In order to avoid the casting problems an adapted very fine casting powder is required that could cause health problems. Steel-making plants are therefore in general not willing to produce this kind of compositions because the workers have to carry masks and a lot of special precautions have to be taken.

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[0006] EP-A-1170391 describes the production of a low carbon (<0.08wt%), low silicon (<0.5wt%) and low aluminium (<0.3wt%) TRIP steel obtained by adding a nitriding step to the processing (0.03-2wt%N). The Al and Si contents have

to be kept low in order to avoid nitride precipitation and thus loss of free N. Furthermore the Si content is preferably lower than 0.2wt% because of hot dip galvanisability. The carbon content is kept very low because of weldability and because of the fact that the presence of nitrogen in the steel also stabilises the retained austenite. This nitrogen is incorporated in the steel sheet either during or immediately after hot finish rolling, during recrystallisation annealing, during intercritical annealing or via a combination of one or more of these processes. All of them require the steel sheet to be held for 2sec to 10min. in an atmosphere containing not less than 2% ammonia in the temperature range 550-800°C. It is clear that this nitriding step makes processing a lot more difficult and requires complicated technical modifications to existing installations. At the moment this process is internationally not considered to be industrially feasible. Furthermore the very low alloying content of this steel grade, does not allow to reach tensile strength levels above 650MPa.

**[0007]** US-A-5470529 deals with the production of cold rolled TRIP steels based upon a wide variety of combined Al-Si analyses. The carbon content range is set as 0.05-0.3wt%, but more preferably is 0.1-0.2wt%. The Si-content is kept below 1.0wt% in order to avoid red scale formation, but more preferably is in the range 0.2-0.9wt%. Manganese is added in 0.005 to 4.0wt%, but more preferably 0.5-2.0wt%. As compared to traditional Si-Mn TRIP compositions, part of the Si is replaced by Al for various reasons. Like Si, Al also avoids cementite precipitation during bainitic holding. This enables to use lower Si-levels and thus avoid red scale formation. Furthermore the addition of Al increases the  $A_{r3}$  temperature, leading to an increased carbon concentration in the austenite phase that is formed during intercritical annealing. This in turn stabilises the retained austenite and makes the steel less susceptible to stress-induced transformation in low stress regions, leading to an improved hole expansion ratio. Therefore the Al-range is set as 0.1-2.0wt% and more preferably as 0.5-1.5wt%. However, as Al and Si are both ferrite stabilizers, their sum is limited in order to avoid over-stabilizing the retained austenite. The Al+Si content should be in the range 0.5-3.0wt% and more preferably in the range 1.5-2.5wt%. In this invention P is considered as an incidental impurity that should be limited as much as possible. The P-limit is set at 0.1wt% or less and preferably less than 0.02wt%. Cu is added to the analysis to facilitate the removal of red scale, to improve the corrosion resistance of the as cold rolled product and to improve the wettability by molten Zn. Therefore the Cu-range is 0.1-2.0wt% and more preferably 0.1-0.6wt%. To avoid hot shortness problems when using Cu, Ni is added as well. For economics its content is limited to 1.0wt% and preferably 0.5wt%. The following constraints also apply:  $Ni(wt\%) > Cu(wt\%)/3$  when  $Cu > 0.5wt\%$  and  $Mn+Ni > 0.5wt\%$ . Cr may be added as well to stabilise the retained austenite and to further improve corrosion resistance. It is added in the range 0.5-5.0wt% and more preferably in the range 0.6-1.6wt%. To increase tensile strength further Ti, Nb and V might be added as well. Their upper limit is preferably 0.05wt% for Nb and Ti and 0.10wt% for V. Although the maximum Si-content in this invention is limited to <1wt% in order to avoid red scale formation, most of the cold rolled example steels have a Si-content in the range 0.5-1.1wt%. The latter is considered to give rise to hot dip galvanising difficulties (bad wettability by molten Zn) and a deteriorated surface appearance (bare spots). None of these example steels contained micro-alloying additions as in high Si-TRIP steels, these are known to markedly increase the hot strip hardness, leading to strongly increased cold rolling forces. The low Si (0.2-0.4wt%) example steels on the other hand showed a high yield stress (570-590MPa) and only moderate ultimate tensile strength ( $\leq 700MPa$ ) and total elongation values ( $A_{50} \leq 30\%$ ). In the latter steels no P was added additionally. A large disadvantage of these compositions is the necessity of adding Cu and Ni, elements which are considered as impurities in bulk flat carbon steel production. If a steelmaking plant has to cast this, extra logistic problems with scrap recycling occur. Moreover, the use of Ni, Cu and Cr makes the alloying cost much more expensive.

**[0008]** EP-A-1154028 describes the manufacturing of a P-alloyed low-Al, low-Si TRIP steel, which contains (in wt%): 0.06-0.17%C, 1.35-1.80%Mn, 0.35-0.50%Si, 0.02-0.12%P, 0.05-0.50%Al, max. 0.07%Nb, max. 0.2%V, max. 0.05%Ti, max. 30ppm B and 100-350ppm N. When the carbide forming elements Ti, Nb or V are added, the carbon content is preferably 0.16wt%. The amount of residual austenite is limited to a maximum of 10%. The combination of low Si-content and rather low C-content, results in tensile strength values which are quite low (<600MPa). When micro-alloying elements are added, the strength level is markedly improved (800MPa), but elongations drop drastically ( $A_{80} < 17\%$ ). Elongation values are in all cases rather low, which can be explained by the limited addition of Al and C, rendering the retained austenite less stable.

**[0009]** L. Barbé et al have studied the influence of phosphorus additions to several TRIP compositions, ranging from pure Si-TRIP steels over combined Al-Si TRIP-steels to pure Al-TRIP steels ("Effect of phosphorus on the properties of a cold rolled and intercritically annealed TRIP-aided steel", Int. Conf. on TRIP-Aided High Strength Ferrous Alloys, Ghent, June 19-21, 2002). They found that the TRIP-aided steel composition which contained (in wt%) 0.24% C, 1.66% Mn, 0.6% Al, 0.4% Si and 0.073% P resulted in an excellent combination of mechanical properties ( $A_{80}=28.4\%$  and  $UTS=788MPa$ ). Lab-experiments performed by the inventors of the present invention have however shown that Al-additions as low as 0.6wt%, render the obtained mechanical properties very sensitive to process parameter variations such as line speed and overageing temperature. This can lead to a non-compatibility between different galvanising lines (with e.g. different lengths of the levelling zone around 490-460°C) or even to strongly thickness-dependent mechanical properties. This can be explained by the insufficient stabilisation of the retained austenite and the shift of



the optimum overageing time to noticeably longer times due to the too low Al-additions.

[0010] O. Yakubovsky et al have studied the stress-strain behaviour and bake hardening behaviour of several TRIP compositions, ranging from pure Si-TRIP steels over combined Al-Si TRIP-steels to pure Al-TRIP steels ("Stress-strain behaviour and bake hardening of TRIP and TRIP-aided multiphase steels", Int. Conf. on TRIP-Aided High Strength Ferrous Alloys, Ghent, June 19-21, 2002). In all cases the carbon content was limited to (in wt%) 0.15% and the manganese content to 1.5%. Amongst the steels studied was also a (in wt%) 0.25-0.45% Si, 1.5-2.0% Al and 0.05-0.10% P TRIP steel. No mechanical properties were mentioned in the article for the latter composition. Based upon the tensile strength versus carbon content relationship that was established from industrial production and laboratory research by the inventors of the present invention, the proposed chemical composition is insufficiently alloyed in carbon to reach tensile strengths in the range 700-850 MPa. Furthermore the high Al-content requires the use of an adapted very fine casting powder that can give rise to health problems. Furthermore the weldability can be impaired due to the presence of Al-oxides in the welded area, a consequence of the high Al-contents.

[0011] S. Papaefthymiou et al. studied the microstructure development and mechanical behaviour of two Al-Si-TRIP steels that were uni-axially deformed to different strain levels directly after intercritical annealing ("Microstructure development and mechanical behaviour of Al-containing TRIP-steels", Int. Conf. on TRIP-Aided High Strength Ferrous Alloys, Ghent, June 19-21, 2002). As a consequence of this special treatment and because of the non-standard sample geometry, the mechanical properties mentioned in the article are not comparable. The two Al containing TRIP steels that were studied can be divided in a low-Al and a high-Al steel. These contain (in wt%): low-Al steel: 0.19% C, 1.5% Mn, 0.26% Si, 0.086% P and 0.52% Al; high-Al steel: 0.17% C, 1.46% Mn, 0.26% Si, 0.097% P and 1.81% Al. As already explained before, the low-Al steel will suffer from mechanical properties that are very sensitive to process parameter variations such as line speed and overageing temperature. This can lead to a non-compatibility between different galvanising lines or even to strongly thickness-dependent mechanical properties. The high-Al steel on the other hand again requires the use of an adapted casting powder that can give rise to health problems. Furthermore the weldability will be impaired due to the presence of Al-oxides in the welded area.

[0012] A. Pichler et al. ("Correlation between thermal treatment, retained austenite stability and mechanical properties of low-alloyed TRIP steels", Int. Conf. on TRIP-Aided High Strength Ferrous Alloys, Ghent, June 19-21, 2002) studied the influence of different annealing process parameters on the retained austenite stability and mechanical properties of a low-alloyed TRIP-steel that contained (in wt%): ~0.2% C, ~1.6% Si+Al, ~1.5% Mn, <0.5% Cr+Mo, <0.04%P, <0.01% S and <0.05% Ti+Nb. As no specifications were given related to the Al/Si ratio in this analysis, it is not possible to conclude about the galvanisability. The mentioned P-content is insufficient for obtaining the desired mechanical properties (high tensile strength in combination with high elongation), whilst maintaining a good weldability (sufficient carbon content reduction).

#### Aims of the invention

[0013] It is the aim of the present invention to provide a high strength, low Si, high Al, P-alloyed TRIP steel composition for the production of steel products, produced by cold rolling that can readily be galvanised. It is a further aim to propose a process for the manufacturing of such products, and to propose finally the products themselves, wherein said composition, said process and said products do not suffer from prior art problems.

#### Summary of the invention

[0014] The present invention is related to a cold rolled Al-Si P-alloyed TRIP steel composition intended to be used as uncoated, electro-galvanised or hot dip galvanised material. Said composition is characterised by the following contents :

- C : between 1300ppm and 2600ppm
- Mn : between 10000ppm and 22000ppm
- Al : between 8000ppm and 15000ppm
- Si : between 2000ppm and 6000ppm
- P : between 400 and 1000ppm
- S : maximum 120ppm
- N : maximum 200ppm
- Ti : maximum 1000ppm
- Nb : maximum 1000ppm
- V : maximum 1000ppm
- B : maximum 10ppm

the remainder being substantially iron and incidental impurities.

[0015] The novelty and inventive step of this composition lies in the specific combination of elements P, Si, Al and C. In particular, adding P in excess of prior art levels, whilst limiting the maximum Si- and Al-content, allows to decrease the C-content for reaching a certain strength level, in combination with better weldability.

[0016] Three specific embodiments are related to the same chemical composition, but having three different sub-ranges for carbon which are related to the strength level that is aimed at:

- UTS (Ultimate Tensile strength)  $\geq$  590MPa : carbon between 1300ppm and 1900ppm
- UTS  $\geq$  690MPa : carbon between 1700ppm and 2300ppm
- UTS  $\geq$  780MPa : carbon between 2000ppm and 2600ppm

[0017] Likewise three specific embodiments are related to the same subranges for carbon content which are related to the strength level that is aimed at, but having furthermore the following specific chemical composition:

- Mn : between 13000ppm and 22000ppm
- Al : between 8000ppm and 14000ppm
- Si : between 2500ppm and 4500ppm
- P : between 600 and 1000ppm
- S : maximum 120ppm
- N : maximum 150ppm
- Ti : maximum 200ppm
- Nb : maximum 100ppm
- V : maximum 100ppm
- B : maximum 5ppm

the remainder being substantially iron and incidental impurities.

[0018] Likewise three more specific embodiments are related to the the same subranges for carbon content which are related to the strength level that is aimed at, but having furthermore the following specific sub-range for aluminium: 9000-1300ppm. The subranges for the other alloying elements are kept the same as in paragraph [0017].

[0019] The present invention is equally related to a process for manufacturing a cold rolled TRIP steel product, comprising the steps of:

- preparing a steel slab having a composition according to the invention,
- hot rolling said slab, wherein the finishing rolling temperature is higher than the Ar3 temperature, to form a hot-rolled substrate,
- cooling said substrate to a coiling temperature (CT) between 500°C and 680°C,
- coiling said substrate at said coiling temperature,
- pickling said substrate to remove the oxides,
- cold rolling said substrate to obtain a reduction of thickness, with a minimum reduction of 40%.

[0020] According to a first embodiment, the process of the invention further comprises the steps of:

- soaking said substrate at a temperature between 760°C and 850°C,
- cooling said substrate with a cooling rate higher than 2°C/s to a temperature in the range 360°C to 450°C,
- holding said substrate in said temperature range for a time less than 700s,
- cooling said substrate to room temperature at a cooling rate higher than 1°C/s.
- subjecting said substrate to a skinpass reduction of maximum 1.5%.

[0021] According to a second embodiment, the process of the invention further comprises an electrolytic zinc coating step.

[0022] According to a third embodiment, the process of the invention further comprises the following processing steps after the cold rolling step:

- soaking said substrate at a temperature between 760°C and 850°C,

- cooling said substrate with a cooling rate higher than 2°C/s to the temperature of a Zn-bath,
- holding said substrate in the temperature range between 490°C and 460°C for less than 200 seconds.
- hot dip galvanising said substrate in said Zn-bath,
- cooling said substrate to room temperature at a cooling rate higher than 2°C/s.

[0023] The process comprising a hot dip galvanising step may further comprise the step of subjecting said substrate to a skinpass reduction of maximum 1.5%.

[0024] The invention is equally related to a steel product produced according to the process of the invention and having a microstructure comprising 30-75% ferrite, 10-40% bainite, 0-20% retained austenite and possibly 0-10% martensite.

[0025] The invention is equally related to a steel product produced according to the process of the invention and having a carbon content between 1300ppm and 1900ppm. Said product has a yield strength between 320MPa and 480MPa, a tensile strength above 590MPa, an elongation A80 higher than 26% and a n-value (this is the strain hardening coefficient, calculated between 10% and uniform elongation) higher than 0.2.

[0026] The invention is further related to a steel product produced according to the process of the invention and having a carbon content between 1700 and 2300ppm. Said product has a yield strength between 350MPa and 510MPa, a tensile strength above 700MPa, an elongation A80 higher than 24% and a n-value (calculated between 10% and uniform elongation) higher than 0.19.

[0027] The invention is further related to a steel product produced according to the process of the invention and having a carbon content between 2000ppm and 2600ppm. Said product has a yield strength between 400MPa and 600MPa, a tensile strength above 780MPa, an elongation A80 higher than 22% and a n-value (calculated between 10% and uniform elongation) higher than 0.18.

[0028] The invention is also related to a steel product produced according to the process of the invention and having a carbon content between 2000 and 2600ppm. Said product has a yield strength between 450MPa and 700MPa, a tensile strength above 980MPa, an elongation A80 higher than 18% and a n-value (calculated between 10% and uniform elongation) higher than 0.14.

[0029] A steel product according to the invention may have a bake hardening BH2 higher than 40MPa in both longitudinal and transversal directions.

#### Detailed description of the preferred embodiments

[0030] According to the present invention, a steel composition is proposed for the production of a P-alloyed Al-Si TRIP steel product. Application of the broadest chemical composition ranges which are indicated, will be able, in combination with the right process parameters, to result in products having a desired TRIP microstructure, good weldability as well as excellent mechanical properties, with very high values of the product of tensile strength and total elongation (this value is characteristic for a high energy absorption potential in case of a crash). The preferred ranges are related to more narrow ranges of mechanical properties, for example a guaranteed minimum tensile strength of 780MPa, or to more stringent requirements on weldability (maximum of C-range, see next paragraph).

[0031] C : between 1300ppm and 2600ppm. A first preferred subrange is 1300-1900ppm. A second preferred sub-range is 1700-2300ppm. A third preferred subrange is 2000-2600ppm. The minimum carbon content per sub-range is needed in order to ensure the strength level as carbon is the most important element for the hardenability. The maximum of the claimed range per sub-range is related to weldability. The effect of carbon on mechanical properties is illustrated by exemplary composition A, E and F and reference compositions B, C and D (tables 1, 3-8). The effect of carbon content on spot weldability is illustrated by reference compositions B, C and D (table 2).

[0032] Mn : between 10000ppm and 22000ppm, preferably between 13000-22000ppm. Manganese acts as an austenite stabiliser and thus decreases the Ms temperature of the retained austenite. Furthermore Mn suppresses pearlite formation and also contributes to the overall strength level of the steel by solid solution hardening. Adding excess Mn results on the other hand in insufficient ferrite formation upon cooling from the soaking temperature and thus to insufficient carbon concentration in the retained austenite, rendering the latter less stable. Too much Mn will also increase the hardness of the weld and will enhance the formation of detrimental banded microstructures.

[0033] Al : between 8000ppm and 15000ppm, preferably between 8000-14000ppm and most preferably between 9000-13000ppm. Aluminium is added because, to an even stronger degree than Si, it is a ferrite stabiliser and thus enhances the ferrite formation during soaking and during cooling from the soaking temperature, thereby stabilising the retained austenite. The latter is stabilised even more by the fact that Al also suppresses the precipitation of carbon from the retained austenite during the overageing stage. Unlike Si, Al has no detrimental effect on galvanisability. Al-contents above 15000ppm are however known to require the use of an adapted very fine casting powder that can cause health problems. Furthermore weldability can deteriorate due to the presence of Al-oxides in the welded area. A minimum Al content is however required to allow the material to be processed on different hot dip galvanising lines



with different lengths of the levelling zones and to ensure a high process robustness.

[0034] Si : between 2000ppm and 6000ppm, preferably between 2500-4500ppm. Silicon has essentially the same function as Al, albeit slightly less pronounced. That is: Si is a ferrite stabiliser and prevents carbide precipitation during the overageing stage, thereby stabilising the retained austenite at room temperature. Besides this, Si also contributes to the overall strength level of the steel by solid solution hardening. The maximum Si-content is however limited as Si is well known to provoke problems as to surface quality because of the presence of Si-oxides which after pickling create a surface with irregular and very high roughness. Moreover, in view of corrosion protection, hot dip galvanising of high Si-containing substrates in general leads to insufficient surface appearance for automotive applications, with moreover a high risk on the presence of bare spots on the surface.

[0035] P : between 400ppm and 1000ppm, preferably between 600-1000ppm. Phosphorous is added primarily to allow the carbon content to be decreased to obtain improved weldability, while maintaining the same tensile strength level. Furthermore, P in combination with Si, is known to enhance the retained austenite stability by suppressing carbide precipitation during the overageing stage. In this respect P additions below 400ppm do not allow a sufficiently large reduction of C-content. When adding more than 1000ppm P, the risk on segregation defects increases and weldability is again deteriorated.

[0036] S : maximum 120ppm. The S-content has to be limited because a too high inclusion level can deteriorate the formability.

[0037] N : maximum 200ppm, preferably maximum 150ppm otherwise too much AlN and/or TiN precipitates can form which are detrimental to formability.

[0038] Ti : maximum 1000ppm, preferably below 200ppm for products produced according to the present invention having a tensile strength below 980MPa. Titanium can be added in order to increase the tensile strength of the steel by grain refinement and precipitation strengthening. However for tensile strengths below 980MPa, even without adding Ti, using the appropriate processing parameters, will result in the targeted mechanical properties per carbon sub-range and thus avoid an increase in analysis cost or extra processing difficulties (e.g. rolling forces).

[0039] Nb : maximum 1000ppm, preferably below 100ppm for products produced according to the present invention having a tensile strength below 980MPa. Niobium can be added in order to increase the tensile strength of the steel by grain refinement and precipitation strengthening. However for tensile strengths below 980MPa, even without adding Nb, using the appropriate processing parameters, will result in the targeted mechanical properties per carbon sub-range and thus avoid an increase in analysis cost or extra processing difficulties (e.g. rolling forces).

[0040] V : maximum 1000ppm, preferably below 100ppm for products produced according to the present invention having a tensile strength below 980MPa. Vanadium can be added in order to increase the tensile strength of the steel by grain refinement and precipitation strengthening. However for tensile strengths below 980MPa, even without adding V, using the appropriate processing parameters, will result in the targeted mechanical properties per carbon sub-range and thus avoid an increase in analysis cost.

[0041] B : maximum 10ppm, preferably maximum 5ppm. Boron is avoided because of its detrimental influence on ferrite nucleation.

[0042] The present invention is equally related to the process for producing said steel product. This process comprises the steps of:

- preparing a steel slab having a composition according to the invention, such as defined above,
- if necessary, reheating said slab to a temperature higher than 1000°C, preferably above 1200°C,
- hot rolling the slab, wherein the finishing rolling temperature FT at the last stand of hot rolling is higher than the Ar3 temperature,
- cooling to coiling temperature CT, preferably by continuous cooling to the CT, typically at 40-50°C/s. Stepwise cooling may be used as well,
- hot rolling mill coiling of said substrate at a coiling temperature CT comprised between 500°C and 680°C, preferably between 600°C and 680°C. This temperature range is chosen so as to create a hot band which is as soft as possible in order to facilitate cold rolling,
- pickling the substrate to remove the oxides,
- cold rolling to obtain a reduction of thickness. The cold rolling reduction is preferably higher than 40%.

[0043] According to a first embodiment of the invention, these steps are followed by an annealing treatment in a continuous annealing line, comprising the following steps:

- soaking said pickled cold rolled substrate in a temperature range between 760 and 850°C in order to create a microstructure that consists of ferrite and austenite. If the soaking temperature is chosen above 850°C, the amount of austenite formed will be too large, which leads to a less stable retained austenite in the end product. Due to the reduced austenite stability, a substantial part of it could also transform to martensite during final cooling to room

temperature which deteriorates elongation properties. If, on the other hand, the soaking temperature would be chosen too low, insufficient austenite would be formed during soaking. This could lead to over-stabilisation of the retained austenite, which again deteriorates mechanical properties.

- Cooling said substrate with a cooling rate higher than 2°C/s to a holding temperature in the range 360°C to 450°C. The holding time in said temperature range is less than 700 seconds. When the holding temperature would be chosen below 360°C, a substantial part of the retained austenite will transform to martensite, leading to a DP-like behaviour (high initial n-value that decreases as a function of increasing strain) of the final product. Holding temperatures above 450°C, will on the other hand lead to a decomposition of the retained austenite by carbon precipitation. This will again deteriorate elongation properties.
- Final cooling of said substrate to a temperature below 150°C with a cooling rate higher than 1°C/.
- Finally said substrate can be subjected to a skinpass reduction which is preferably in the range 0.3% to 1.5%.

**[0044]** A second preferred embodiment comprises the same processing steps mentioned above, but additionally also comprises an electrolytic zinc coating step.

**[0045]** According to a third embodiment of the invention, the cold rolling step is followed by an annealing treatment in a continuous hot dip galvanising line, comprising the following steps:

- soaking said pickled cold rolled substrate in a temperature range between 760 and 850°C in order to create a microstructure that consists of ferrite and austenite. If the soaking temperature is chosen above 850°C, the amount of austenite formed will be too large, which leads to a less stable retained austenite in the end product. Due to the reduced austenite stability, a substantial part of it could also transform to martensite during final cooling to room temperature which deteriorates elongation properties. If, on the other hand, the soaking temperature would be chosen too low, insufficient austenite would be formed during soaking. This could lead to over-stabilisation of the retained austenite, which again deteriorates mechanical properties.
- cooling said substrate with a cooling rate higher than 2°C/s to the temperature of the Zn-bath,
- holding said substrate in the temperature range between 490°C and 460°C for less than 200 seconds and preferably between 5 seconds and 80 seconds.
- hot dip galvanising said substrate in said Zn-bath,
- final cooling to room temperature at a cooling rate higher than 2°C/s.
- Finally said substrate can be subjected to a skinpass reduction which is preferably in the range 0.3% to 1.5%.

**[0046]** The thickness of the steel substrates of the invention after cold rolling can be lower than 1mm according to the initial hot rolled sheet thickness and the capability of the cold rolling mill to perform the cold rolling at a sufficiently high level. Thus, thicknesses between 0.3 and 2.5mm are feasible.

**[0047]** The resulting cold rolled product has a multiphase structure with 30-75% ferrite, 10-40% bainite, 0-20% retained austenite and possibly amounts of martensite (0-10%) present at room temperature. The amount of martensite at room temperature should however be limited in order to maintain an n-value behaviour (constant or increasing with strain) and mechanical properties that are characteristic for TRIP-steels. Specific mechanical properties as a function of processing parameter values are given in the examples.

**[0048]** The cold rolled non-temper rolled product showed in all cases a yield point elongation, which is typical for TRIP-steels and indicates that no or only very small amounts of martensite are present in the microstructure. This yield point elongation can be suppressed by temper rolling the final product. Small temper rolling reductions are sufficient to avoid the occurrence of a yield point elongation and temper rolling reductions above 1.5% should be avoided in order to prevent a too large yield strength increase.

**[0049]** The final cold rolled product furthermore preferably exhibits a constant or increasing n-value with increasing strain. This behaviour implies that the retained austenite is gradually transformed into martensite as the tensile test progresses thereby postponing the occurrence of necking, leading to an excellent combination of tensile strength and total elongation.

**[0050]** The robustness of TRIP steel products produced according to this invention is ensured by the minimum Al-content specified in the preferred Al-range: 8000-14000ppm and most preferably in the range 9000-13000ppm. Adding less Al will render the retained austenite less stable. This will increase the risk of loss of mechanical properties by austenite decomposition through carbon precipitation and on the other hand the less stable retained austenite will more easily transform into martensite during straining, limiting the formability of the material. Adding less Al will also retard the bainite transformation kinetics. As a consequence the mechanical properties will become more dependent on processing conditions such as line speed and overageing temperature as well on the actual line lay-out (short or long overageing section). Using an Al-content within the preferred range, avoids such line dependency and loss of robustness.

**[0051]** Concerning weldability of the obtained cold rolled product, the addition of phosphorus allows to decrease the



carbon content as compared to P-free Al-Si TRIP steels of the same tensile strength level. As in the investigated carbon range, weldability is improved by lowering the carbon content, such a carbon content reduction by P-addition can be considered as the main advantage of the current invention.

[0052] The different drawbacks described above as to the compositions described in state of the art publications are not encountered when the composition of the present invention is applied:

- Si is limited in order to ensure the hot dip galvanisability. The surface appearance of the hot dip galvanised cold rolled steel of the present invention is sufficient for automotive unexposed applications whereas substrates with higher Si-contents in general lead to insufficient surface appearance for automotive applications, with moreover a much higher risk on the presence of bare spots on the surface.
- Si is furthermore limited in order to avoid the need of hot charging the slabs to prevent crack formation.
- The presence of red scale on the hot rolled substrate's surface is also avoided by limiting the Si-content.
- A small amount of Si, which is compatible with hot dip galvanising, is added to more easily reach the targeted tensile strength levels. In comparison with Si-free Al-TRIP steels, this allows to use a lower C-content or lower Al-content.
- The maximum Al-content is limited to avoid the use of an adapted very fine casting powder that could cause health problems. Furthermore in the case of high Al-contents (>1.5%) weldability could deteriorate due to the presence of Al-oxides in the welded area. A minimum Al-content however ensures a high process robustness and less sensitivity to changes in line speed, overageing temperature and lay-out of the continuous annealing or hot dip galvanising line.
- For a given tensile strength level, the C content is limited as compared to other Al-Si TRIP steels in order to improve weldability, by the addition of P and without the need of micro-alloying.
- No Ni, Cu or Cr are added to the steel products of the invention. This avoids logistic problems with scrap recycling and reduces the cost of the analysis.

#### Detailed description of preferred embodiments - examples

##### 1. Example compositions

[0053] Table 1 shows examples of compositions of laboratory castings of the P-alloyed Al-Si TRIP steel product according to the present invention (codes A, E and F), and of reference compositions (B,C and D) having either a C-content which is higher than the claimed range and/or no intentionally added phosphor. Laboratory thermal cycle simulations and tensile tests were performed to obtain the mechanical properties of the test specimens of these example compositions. It is to be noted that in what follows, all mentioned tensile test mechanical properties are measured according to the standard EN10002-1.

##### 1.1 Cold rolled and continuously annealed product

[0054] The processing steps were:

- Casting,
- Reheating at 1250°C for 1 hour,
- Hot rolling in the austenite region to a final thickness of 3.5 mm,
- Water cooling to the coiling temperature of 600°C,
- Cold rolling to a final thickness of 1 mm,

[0055] After the previous processing steps, tensile specimens with 80 mm gauge length parallel to the rolling direction were machined out of the sheets. These specimens were heat treated in two salt baths following a two-step thermal cycle. After annealing in the intercritical region (IAT) for a given time (IAt), the samples were quenched in a salt bath at a lower temperature and isothermally held (BHT) for a given time (BHt). The mechanical properties are listed in table 3 and are conform the specifications for a TRIP700 grade. No temper rolling was applied. When comparing the mechanical properties mentioned in table 3 (example composition A), with those mentioned in table 5 (in particular reference composition C), it becomes clear that the addition of P in the steel of the present invention clearly allows to reduce the carbon content with 500ppm while maintaining the tensile strength level. This C-reduction will seriously improve weldability (cfr. Table 2: difference between 0.25C and 0.20C). Table 7 contains the mechanical properties obtained after applying several continuous annealing simulations on steel samples of compositions E and F. Looking at the data in table 5 and 7 (in particular E compared to B), it is clear that the tensile strength is even higher for the composition of the invention, as compared to the reference composition which has 600ppm more carbon and no intentionally added

phosphor.

1.2 Cold rolled and hot dip galvanised product

5 [0056] The processing steps were:

- Casting,
- Reheating at 1250°C for 1 hour,
- Hot rolling in the austenite region to a final thickness of 3.5 mm,
- 10 - Water cooling to the coiling temperature of 600°C,
- Cold rolling to a final thickness of 1 mm.

[0057] After the previous processing steps, tensile specimens with 80 mm gauge length parallel to the rolling direction were machined out of the sheets. These specimens were heat treated in two salt baths following a two-step thermal cycle. After annealing in the intercritical region, the samples were quenched in a salt bath at a lower temperature and isothermally held. The temperatures and holding times were adapted in order to simulate closely the process steps, including a hot dip galvanizing step. The mechanical properties are listed in table 4 and clearly illustrate that the current invention leads to a very robust hot dip galvanized TRIP700 product : a broad variation of process parameters (IAT, lat, BHT, BHt) all result in products with comparable mechanical properties. No temper rolling was applied. When  
20 comparing the mechanical properties mentioned in table 4 (example composition A), with those mentioned in table 6 (in particular reference composition C), it becomes clear that the addition of P in the steel of the present invention clearly allows to reduce the carbon content with 500ppm while maintaining the tensile strength level. This C-reduction will seriously improve weldability (cfr. Table 2).

[0058] Table 8 contains the mechanical properties obtained after applying several hot dip galvanising simulations on steel samples of compositions E and F. Looking at the data in table 6 and 8 (in particular E compared to B), it is clear that the tensile strength is even higher for the composition of the invention, as compared to the reference composition which has 600ppm more carbon and no intentionally added phosphor.

Code	C	Mn	Al	Si	P	S	N	As	Nb	V
A	2000	16200	9000	3000	850	20	69	20	20	30
B	3000	15000	12000	3000	173	60	43	17	30	43
C	2500	15000	12000	3000	167	55	32	37	26	45
D	2000	15000	10000	3000	223	32	48	36	38	55
E	2400	15100	11200	2700	820	10		100	50	
F	2200	15000	13400	4400	730	10		50	50	

Table 1 : Compositions (ppm) of Al-Si TRIP steels. Compositions A, E, F according to the invention, B, C and D are reference compositions.

Code	Fmax at Imax (N)
B	6906
C	7489
D	9608

Table 2: Average of max. force measured at Imax in cross-tensile test on spot welds according to AFNOR-A87001.



Table 3:

Mechanical properties of the cold rolled and continuously annealed P-alloyed Al-Si TRIP steel, composition A, according to the present invention. No temper rolling applied. Thickness 1mm.

Code	IAT (°C)	IAt (s)	BHT (°C)	BHt (s)	Rp0.2 (MPa)	Rm (MPa)	Au (%)	A80 (%)
A	770	60	400	120	486	708	24.7	30.9

Table 4 :

Mechanical properties of the cold rolled and hot dip galvanised P-alloyed Al-Si TRIP steel, composition A, according to the present invention. No temper rolling applied. Thickness 1mm. (BH = bainitic holding = holding before passing through the zinc bath)

IAT (°C)	IAt (s)	BHT (°C)	BHt (s)	Rp0.2 (MPa)	Rm (MPa)	Au (%)	A80 (%)	Re/Rm	RmxA80
770	73	460	20	411	738	23.6	28.6	0.557	21107
		490		408	756	22.6	28.0	0.540	21168
800		460		436	756	24.2	29.6	0.577	22378
		490		428	775	22.5	28.1	0.552	21778
830		460		427	746	24.6	30.2	0.572	22529
		490		434	761	22.4	28.1	0.570	21384
770	52	460	14	419	734	24.3	29.4	0.571	21580
		490		419	754	22.5	27.2	0.556	20509
800		460		432	755	23.7	28.8	0.572	21744
		490		427	760	23.1	28.3	0.562	21508
830		460		427	748	22.7	27.8	0.571	20794
		490		428	771	21.7	27.0	0.555	20817
770	36	460	10	423	701	24.7	30.3	0.603	21240
		490		419	726	23.8	28.7	0.577	20836
800		460		433	755	23.9	28.9	0.574	21820
		490		426	743	22.0	26.8	0.573	19912
830		460		441	768	23.6	28.9	0.574	22195
		490		449	765	23.0	27.9	0.587	21344

Table 5:

Mechanical properties of the cold rolled and continuously annealed reference Al-Si TRIP steels. (RD: rolling direction; TD: transverse direction)

Code	Thickness (mm)	SKP (%)	Re (MPa)		Rm (MPa)		A80 (%)	
			RD	TD	RD	TD	RD	TD
B	1	0.50	508	499	737	726	34.0	32.0
	1.5	0.75	508	500	732	746	31.0	27.0
	1.6	1.00	524	515	737	745	31.0	29.0

Table 5: (continued)

Mechanical properties of the cold rolled and continuously annealed reference Al-Si TRIP steels. (RD: rolling direction; TD: transverse direction)								
Code	Thickness (mm)	SKP (%)	Re (MPa)		Rm (MPa)		A80 (%)	
			RD	TD	RD	TD	RD	TD
C	0.7	0.50	502	499	713	717	34.3	32.1
	1.45	0.80	507	496	692	700	34.2	31.5
D	0.85	0.70	483	463	664	668	27.8	29.2
	1.22	0.70	451	451	647	657	30.1	29.9
	1.47	0.75	466	457	650	658	28.5	27.7

Table 6 :

Mechanical properties of the hot dip galvanised reference Al-Si TRIP steels. (RD: rolling direction; TD: transverse direction)								
Code	Thickness (mm)	SKP (%)	Re (MPa)		Rm (MPa)		A80 (%)	
			RD	TD	RD	TD	RD	TD
B	1.00	0.5	490	482	800	803	32.1	30.1
	1.2	0.7	483	485	802	810	32.7	30.7
C	1.00	0.6	458	449	727	732	34.6	35.4
	1.45	0.9	472	462	732	727	33.2	31.4
D	1.49	1.0	446	438	652	647	33.8	30.9
	1.23	1.1	451	456	673	675	32.8	33.0

Table 7 :

Mechanical properties of the cold rolled and continuously annealed P-alloyed Al-Si TRIP steel, compositions E and F, according to the present invention. No temper rolling applied. Thickness 1mm.									
Code	IAT (°C)	IAt (s)	BHT (°C)	BHt	Rp0.2 (MPa)	Rm (MPa)	A80 (%)	Re/Rm	RmxA80
E	800	209	375	448	595	820	26.1	0.726	21402
			425		593	795	33.2	0.746	26394
		125	375	280	562	834	26.9	0.674	22434
			425		589	798	27.3	0.738	21785
F	800	209	375	448	597	837	27.5	0.713	23017
			425		582	819	32	0.710	26208
		125	375	280	569	855	27.3	0.665	23341
			425		589	820	32.4	0.718	26568

Table 8:

Mechanical properties of the cold rolled and hot dip galvanised P-alloyed Al-Si TRIP steel, compositions E and F, according to the present invention. No temper rolling applied. Thickness 1mm. (BH = bainitic holding = holding before passing through the zinc)									
Code	IAT (°C)	IAt (s)	BHT (°C)	BHt (s)	Rp0.2 (MPa)	Rm (MPa)	A80 (%)	Re/Rm	RmxA80
E	800	73	460	20	496	862	26.9	0.575	23188
			490		481	901	24.6	0.534	22165
		45	460	65	544	858	28.3	0.634	24281
			490		528	872	24.3	0.606	21190
		36	460	10	555	799	24.4	0.695	19496
			490		526	881	27.9	0.597	24580
		22	460	32	490	872	23.6	0.562	20579
			490		549	850	27.8	0.646	23630
		73	460	20	487	924	25.1	0.527	23192
			490		437	971	22.1	0.450	21459
F	800	45	460	65	551	830	29.9	0.664	24817
			490		509	938	25.3	0.543	23731
		36	460	10	552	855	27.7	0.646	23684
			490		480	922	24.7	0.521	22773
		22	460	32	480	920	24.9	0.522	22908
			490		532	881	25.8	0.604	22730

### Claims

1. A steel composition intended to be used in a process comprising a cold rolling step, for the production of uncoated, electro-galvanised or hot dip galvanised TRIP steel products, said composition being characterised by the following contents :

- C : between 1300ppm and 2600ppm,
- Mn : between 10000ppm and 22000ppm,
- Al : between 8000ppm and 15000ppm,
- Si : between 2000ppm and 6000ppm,
- P : between 400 and 1000ppm,
- S : maximum 120ppm,
- N : maximum 200ppm,
- Ti : maximum 1000ppm,
- Nb : maximum 1000ppm,
- V : maximum 1000ppm,
- B : maximum 10ppm.

the remainder being substantially iron and incidental impurities.

2. The steel composition according to claim 1, comprising a carbon content between 1300ppm and 1900ppm.
3. The steel composition according to claim 1, comprising a carbon content between 1700ppm and 2300ppm.
4. The steel composition according to claim 1, comprising a carbon content between 2000ppm and 2600ppm.



5. The steel composition according to either one of claims 2, 3 or 4, comprising :

- Mn : between 13000ppm and 22000ppm,
- Al : between 8000ppm and 14000ppm,
- Si : between 2500ppm and 4500ppm,
- P : between 600 and 1000ppm,
- S : maximum 120ppm,
- N : maximum 150ppm,
- Ti : maximum 200ppm,
- Nb : maximum 100ppm,
- V : maximum 100ppm,
- B : maximum 5ppm.

6. The steel composition according to claim 5, comprising an aluminium content between 9000ppm and 13000ppm.

7. A process for manufacturing a cold rolled TRIP steel product, comprising the steps of:

- preparing a steel slab having a composition according to any one of claims 1 to 6,
- hot rolling said slab, wherein the finishing rolling temperature is higher than the Ar3 temperature, to form a hot-rolled substrate,
- cooling said substrate to a coiling temperature (CT) between 500°C and 680°C,
- coiling said substrate at said coiling temperature,
- pickling said substrate to remove the oxides,
- cold rolling said substrate to obtain a reduction of thickness, with a minimum reduction of 40%.

8. The process according to claim 7, further comprising the steps of:

- soaking said substrate at a temperature between 760°C and 850°C,
- cooling said substrate with a cooling rate higher than 2°C/s to a temperature in the range 360°C to 450°C,
- holding said substrate in said temperature range for a time less than 700s,
- cooling said substrate to room temperature at a cooling rate higher than 1°C/s.
- subjecting said substrate to a skinpass reduction of maximum 1.5%.

9. The process according to claim 8, further comprising an electrolytic zinc coating step.

10. The process according to claim 7, further comprising the following processing steps:

- soaking said substrate at a temperature between 760°C and 850°C,
- cooling said substrate with a cooling rate higher than 2°C/s to the temperature of a Zn-bath,
- holding said substrate in the temperature range between 490°C and 460°C for less than 200 seconds.
- hot dip galvanising said substrate in said Zn-bath,
- cooling said substrate to room temperature at a cooling rate higher than 2°C/s.

11. The process according to claim 10, further comprising the step of subjecting said substrate to a skinpass reduction of maximum 1.5%.

12. A steel product produced according to the process of any of claims 8 to 11 and having a microstructure comprising 30-75% ferrite, 10-40% bainite, 0-20% retained austenite and possibly 0-10% martensite.

13. A steel product produced according to the process of any one of claims 8 to 11, said product comprising a carbon content between 1300ppm and 1900ppm, said product having a yield strength' between 320MPa and 480MPa, a tensile strength above 590MPa, an elongation A80 higher than 26% and a strain hardening coefficient, calculated between 10% and uniform elongation, higher than 0.2.

14. A steel product produced according to the process of any one of claims 8 to 11, said product comprising a carbon content between 1700ppm and 2300ppm, said product having a yield strength between 350MPa and 510MPa, a tensile strength above 700MPa, an elongation A80 higher than 24% and a strain hardening coefficient, calculated between 10% and uniform elongation, higher than 0.19.

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15. A steel product produced according to the process of any one of claims 8 to 11, said product comprising a carbon content between 2000ppm and 2600ppm, said product having a yield strength between 400MPa and 600MPa, a tensile strength above 780MPa, an elongation A80 higher than 22% and a strain hardening coefficient, calculated between 10% and uniform elongation, higher than 0.18.

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16. A steel product produced according to the process of any one of claims 8 to 11, said product comprising a carbon content between 2000ppm and 2600ppm, said product having a yield strength between 450MPa and 700MPa, a tensile strength above 980MPa, an elongation A80 higher than 18% and a strain hardening coefficient, calculated between 10% and uniform elongation, higher than 0.14.

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17. A steel product produced according to any one of claims 12 to 16, having bake hardening BH2 higher than 40MPa in both longitudinal and transversal directions.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 02 44 7265

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